

JIS

JAPANESE INDUSTRIAL STANDARD

**Methods for Chemical Analysis
of Calcium-Silicon**

JIS G 1324—1989

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by

Japanese Standards Association

In the event of any doubt arising,
the original Standard in Japanese is to be final authority.

1. Scope

This Japanese Industrial Standard specifies the methods for determination of calcium, silicon, carbon and phosphorus contained in calcium-silicon.

2. General Matters

General matters commonly governing the methods for chemical analysis shall be in accordance with JIS G 1301.

3. Method for Determination of Calcium

3.1 Classification of Determination Methods The determination of calcium shall be in accordance with either of the following methods.

- (1) Potassium Permanganate Titrimetric Method of Precipitated Calcium Oxalate after Iron-Separation This method can be applied to the whole range of calcium content in calcium-silicon.
- (2) Disodium Ethylenediaminetetraacetate Titrimetric Method after Iron-Separation This method can be applied to the whole range of calcium content in calcium-silicon.

3.2 Potassium Permanganate Titrimetric Method of Precipitated Calcium Oxalate after Iron-Separation

3.2.1 Summary Decompose the sample by adding nitric acid and hydrofluoric acid, add perchloric acid, and heat it to generate white fume. After dissolving salts with hydrochloric acid, precipitate and separate iron and the like by neutralizing with aqueous ammonia, and then precipitate calcium oxalate by adding ammonium oxalate. Dissolve this precipitate in sulfuric acid, and titrate the solution with potassium permanganate standard solution.

Applicable Standards:

JIS G 1301-General Rules for Chemical Analysis of Ferroalloys

JIS K 8001-General Rules of Testing Methods for Reagents

JIS Z 2615-General Rules for Determination of Carbon in Metallic Materials

3.2.2 Reagents Reagents shall be as follows.

- (1) Hydrochloric acid (1+1, 1+10)
- (2) Nitric acid (1+1)
- (3) Perchloric acid (60 wt %)
- (4) Hydrofluoric acid
- (5) Sulfuric acid (1+4)
- (6) Aqueous ammonia (1+1)
- (7) Ammonium chloride
- (8) Ammonium chloride solution Dissolve 20 g of ammonium chloride in 1 l of water, add methyl red solution as an indicator, and then drip aqueous ammonia (1+1) until the solution turns yellow.
- (9) Ammonium oxalate solution (saturated, about 40 g/l)
- (10) Ammonium oxalate solution (5 g/l)
- (11) 0.02 mol/l potassium permanganate standard solution (3.161 g KMnO_4 /l) The methods of preparation, storing and standardization shall be in accordance with 4.4 (9) of JIS K 8001.
- (12) Methyl Red Solution Preparation shall be as shown in 4.3 of JIS K 8001.

3.2.3 Quantity of Sample Weigh out a sample of 0.20 g.

3.2.4 Operation

3.2.4.1 Decomposition of Sample Weigh out the sample in a platinum dish (No. 100), add 10 ml of nitric acid (1+1), cover it with a watch glass made of polyethylene or platinum, and decompose it by adding drop by drop about 5 ml of hydrofluoric acid. If this reaction becomes too violent, cool it with water during decomposition. Remove the watch glass while rinsing it with water and, after adding 5 ml of perchloric acid, heat to dryness on a sand bath to generate white fume of perchloric acid. Successively heat it to almost complete dryness. After cooling, add 30 ml of warm hydrochloric acid (1+10) to dissolve soluble salts, and transfer the solution to a beaker (300 ml) while rinsing the dish with water.

3.2.4.2 Separation of Iron or Others Add about 2 g of ammonium chloride and a few drops of the methyl red solution (3.2.2. (12)) as an indicator to the solution obtained in 3.2.4.1, and add bit by bit aqueous ammonia (1+1) while stirring until the solution turns yellow. After boiling it for about 5 min, filtrate the solution through a filter paper (Grade 5 A), and put the filtrate in a beaker (300 ml) to store as a main solution. Wash the precipitate remaining on the filter paper into the former beaker with a

small amount of warm hydrochloric acid (1+10), further wash the paper several times with warm hydrochloric acid (1+10) and then likewise several times with warm water. Put the washings into the beaker already containing the precipitate. After dissolving the precipitate by heating, generate the precipitate as above-mentioned by dripping a few drops of the methyl red solution [3.2.2 (12)] as an indicator, and filtrate it. Wash the precipitate with warm ammonium chloride solution [3.2.2 (8)], and join these washings and filtrate with the main solution.

3.2.4.3 Generation, Filtration and Washing of Precipitate Add hydrochloric acid (1+1) to the solution obtained in 3.2.4.2 until the solution turns red, and heat to concentrate to about 150 ml. Add 20 ml of warm ammonium oxalate solution (saturated), further add bit by bit aqueous ammonia (1+1) while stirring to generate precipitate until the solution turns yellow, heat for about 2 h on a water bath and cool. Filtrate the precipitate through a filter paper (Grade 5 B), and wash it a few times with ammonium oxalate solution (5 g/l) and then wash 5 or 6 times with cold water.

3.2.4.4 Titration Transfer the precipitate obtained in 3.2.4.3 to the former beaker while washing with water, and wash the filter paper first with 25 ml of warm sulfuric acid (1+4) and then about five times with warm water. Put the washings into the former beaker. Dilute the solution with warm water to about 250 ml, heat up to about 80°C and titrate the solution with the 0.02 mol/l potassium permanganate standard solution [3.2.2 (11)] to find the end point when the solution turns pale pink.

3.2.5 Blank Test Carry out the blank test as described in 3.2.4.1 to 3.2.4.4 using only reagents concurrently with the procedures for sample.

3.2.6 Calculation Calculate the calcium content in the sample from the following formula.

$$\text{Calcium wt \%} = \frac{(V_1 - V_2) \times F \times 0.002004}{m} \times 100$$

where, V_1 : consumed volume of 0.02 mol/l potassium permanganate standard solution obtained in 3.2.4.4 (ml)

V_2 : consumed volume of 0.02 mol/l potassium permanganate standard solution obtained in 3.2.5 (ml)

F : factor of 0.02 mol/l potassium permanganate standard solution

m : weighed-out quantity of sample (g)

3.3 Disodium Ethylenediaminetetraacetate Titrimetric Method after Iron-Separation

3.3.1 Summary Decompose the sample with hydrochloric acid and nitric acid, add perchloric acid and heat it to generate white fume. After dissolving the salts in hydrochloric acid, precipitate to eliminate iron and the like by neutralizing with aqueous ammonia, and control its pH with the addition of potassium hydroxide. Add 1-(2-hydroxy-4-sulfo-1-naphthylazo)-2-naphthol-3-carboxylic acid (hereafter referred to as the "NN") as an indicator, and titrate the solution with disodium ethylenediaminetetraacetate standard solution.

3.3.2 Reagents The reagents shall be as follows.

- (1) Hydrochloric acid (1+1, 1+10)
- (2) Nitric acid (1+1)
- (3) Perchloric acid (60 wt %)
- (4) Hydrofluoric acid
- (5) Potassium hydroxide solution (450 g/l)
- (6) Aqueous ammonia (1+1)
- (7) Magnesium hydroxide milk Dissolve 5 g of magnesium chloride hexahydrate in 240 ml of water, add 10 ml of sodium hydroxide solution (200 g/l) and violently agitate this solution into a emulsified state.
- (8) Ammonium chloride
- (9) Ammonium chloride solution (20 g/l) Dissolve 20 g of ammonium chloride in 1 l of water, add the methyl red solution as an indicator, and drip aqueous ammonia until the solution turns yellow.
- (10) Hydroxylammonium chloride solution (60 g/l)
- (11) 0.01 mol/l disodium ethylenediaminetetraacetate (hereafter referred to as "EDTA") standard solution (3.722 g of $C_{10}H_{14}O_8N_2Na_2 \cdot 2H_2O/l$) The methods of preparation and standardization shall be in accordance with 4.4 (5.3) of JIS K 8001.
- (12) NN indicator Mix 0.2 g of NN and 20 g of potassium nitrate, and grind satisfactorily.
- (13) HNB indicator Mix and grind satisfactorily 0.2 g of sodium 1-(2-hydroxyl-4-sulfo-1-naphthylazo)-2-naphthol-3, 6-disulphonate and 20 g of potassium nitrate.
- (14) Methyl red solution

3.3.3 Weighing out Quantity of Sample The sample of 0.20 g shall be weighed out.

3.3.4 Operation

3.3.4.1 Decomposition of Sample Weigh out the sample into a platinum dish (No. 100), add 10 ml of nitric acid (1+1), cover with a watch glass made of platinum or polyethylene and decompose by adding drop by drop about 5 ml of hydrofluoric acid. If this reaction becomes too violent, cool it with water during decomposition. Remove the watch glass while rinsing it with water, add 5 ml of perchloric acid and heat to dryness on a sand bath to generate white fume of perchloric acid. Successively heat it to almost complete dryness. After cooling, add 30 ml of warm hydrochloric acid (1+10) to dissolve soluble salts, and transfer the solution to a beaker (300 ml) while rinsing the dish with water.

3.3.4.2 Separation of Iron and Others Add about 2 g of ammonium chloride and a few drops of the methyl red solution [3.3.2 (14)] as an indicator to the solution obtained in 3.3.4.1, and add bit by bit aqueous ammonia (1+1) while stirring until the solution turns yellow. After boiling it for about 5 min, filtrate the solution through a filter paper (Grade 5 A), and put the filtrate in a 250-ml volumetric flask to store as a main solution. Wash the precipitate remaining on the filter paper into the former beaker with a small amount of warm hydrochloric acid (1+10), and further wash the paper several times with warm hydrochloric acid (1+10) and then likewise several times with warm water. After dissolving the precipitate by heating, generate the precipitate as above-mentioned by dripping a dew drops of the methyl red solution [3.2.2 (12)] as an indicator, and filtrate it. Put the filtrate and washings into the 250-ml volumetric flask already containing the main solution, and wash the precipitate on the filter paper 5 or 6 times with warm ammonium chloride solution [3.3.2 (9)]. After cooling to room temperature, dilute the solution with water up to the marked line.

3.3.4.3 Titration Pipette 25 ml of an aliquot from the solution obtained in 3.3.4.2 into an Erlenmeyer flask (300 ml), dilute it with water up to 50 ml, add 4 ml of potassium hydroxide solution all the while agitating and allow it to stand for 3 or 4 min.

Further add 5 ml of hydroxylammonium chloride solution and about 0.1 g of NN indicator [3.3.2 (12)] or HNB indicator [3.3.2 (13)], and titrate the solution with 0.01 mol/ EDTA standard solution [3.3.2 (11)]. When the color of the solution turns from reddish violet to yellow, add about 4 ml of magnesium hydroxide milk [3.3.2(7)]⁽¹⁾, continue to titrate and take the time when the solution turns blue as the end point.

Note (1) The color change shown at the titration end point becomes more conspicuous by the addition of magnesium hydroxide milk.

3.3.5 Blank Test Carry out the blank test as described in 3.3.4.1 to 3.3.4.3 using only reagents concurrently with procedures for sample.

3.3.6 Calculation Calculate the calcium content in the sample form the following formula.

$$\text{Calcium wt \%} = \frac{(V_1 - V_2) \times F \times 0.0004008}{m \times B} \times 100$$

where, V_1 : consumed volume of 0.01 mol/l EDTA standard solution obtained in 3.3.4.3 (ml)

V_2 : consumed volume of 0.01 mol/l EDTA standard solution obtained in 3.3.5 (ml)

F : factor of 0.01 mol/l EDTA standard solution

m : weighed-out quantity of sample (g)

B : aliquot ratio for sample solution and blank solution

4. Method for Determination of Silicon

4.1 Classification of Determination Methods The methods for determination of silicon shall be in accordance with either of the following methods.

- (1) Silicon Dioxide Gravimetric Method This method can be applied to the whole range of silicon content in calcium silicon.
- (2) Sodium Hydroxide Titrimetric Method after Separation of Precipitated Potassium-Hexafluorosilicate This method can be applied to the whole range of silicon content in calcium-silicon.

4.2 Silicon Dioxide Gravimetric Method

4.2.1 Summary Fuse the sample with fusing mixture or sodium hydroxide, add hydrochloric acid and perchloric acid, and heat it to evaporate to change silicon into insoluble silicic acid. Weigh its weight after igniting the precipitate, treat it with hydrofluoric acid to evaporate silicon dioxide, and then measure its weight.

4.2.2 Reagents The reagents shall be as follows.

- (1) Hydrochloric acid
- (2) Hydrochloric acid (1+1, 1+2, 1+10)
- (3) Perchloric acid (60 wt %)
- (4) Hydrofluoric acid
- (5) Sulfuric acid (1+1, 1+3)
- (6) Sodium hydroxide
- (7) Fusing mixture [sodium peroxide 2, sodium carbonate (unhydride)1]

(8) Potassium thiocyanate solution (100 g/l)

4.2.3 Quantity of Sample Weigh out 0.20 g of sample.4.2.4 Operation4.2.4.1 Decomposition of Sample The sample shall be decomposed by either of the following methods.

- (1) Case of Fusing with Fusing Mixture Weigh out the sample in a nickel crucible (30 ml) or a zirconium crucible (30 ml), adequately mix the sample with 5 g of fusing mixture, and cover the mixed with 1 g of fusing mixture. With a lid on, first heat the crucible at low temperature while rotating it until the inside melts down. Then heat the crucible at about 700°C (dark red) for about 5 min while rotating it to fuse the content completely, and let it cool down. Put the crucible with the lid on in a beaker (500 ml) already containing 60 ml of hydrochloric acid (1+2) to dissolve the fused, and then draw out the crucible and the lid while rinsing with water.
- (2) Case of Fusing with Sodium Hydroxide Weigh out the sample in a nickel crucible (30 ml) or a zirconium crucible (30 ml), adequately mix the sample with 5 g of sodium hydroxide, and satisfactorily dehydrate it on a hot plate, cover with a lid, and heat gradually and carefully to fuse the mixed. After cooling, put the crucible and the lid in a polyethylene beaker (300 ml) already containing about 100 ml of warm water to dissolve the fused, and then draw out the crucible and the lid while rinsing with water. After cooling the solution down to room temperature, transfer it into a beaker (500 ml) already containing 20 ml of hydrochloric acid while rinsing with water.

4.2.4.2 Dehydration Treatment of Solicic Acid Add 40 ml of perchloric acid to the solution obtained in 4.2.4.1, and heat the solution to evaporate on a sand bath until white dense fume is generated. Cover it with a watch glass, continue to heat it for about 15 min under the condition that the vapor of perchloric acid is being refluxed along the inside walls of the beaker. After cooling, add 20 ml of hydrochloric acid (1+1) and about 100 ml of warm water to dissolve soluble salts. Remove the watch glass while rinsing it with water, immediately filtrate the solution through a filter paper (Grade 5 A), and put the filtrate into another beaker (500 ml). Remove the precipitate adhering to the inside of the beaker or the watch glass by rubbing with a policeman (rubber-capped glass rod) while rinsing them with warm hydrochloric acid (1+10), transfer them to the tops of the filter paper, and then wash the paper five times with warm hydrochloric acid (1+10) and next with warm water until no iron ion is detected⁽²⁾. Store the precipitate together with the filter paper as the main precipitate.

Note (2) Continue to wash the paper until no (orange) red color is indicated when potassium thiocyanate solution is added to a small quantity of the washings taken.